UDC 666.3-183.2:678.744.32

FLOW PROPERTIES OF MAJOLICA SLIP WITH A THINNING ADDITIVE BASED ON SODIUM POLYACRYLATE

N. S. Yugai[1] and E. V. Klimova[1]

Translated from Steklo i Keramika, No. 1, pp. 19 – 21, January, 2004.

The effect of a new thinning agent, namely 40% sodium polyacrylate (SPA), on flow properties of majolica slip and the effect of hardness of water on changes in suspension moisture are considered. The use of 40% SPA makes it possible to reduce its content in slip by nearly half, compared to sodium silicate solution, to improve the slip flow properties, and to insignificantly decrease its moisture. An optimum content of 40% SPA in thinning a polymineral clay slip from the Gzhel'skoe deposit and a majolica mixture is determined.

Casting is the main method for making fancy ceramic products of complex shapes. Manual casting, in contrast to other methods for molding ceramic articles, has its own specifics: low efficiency and low turnover of gypsum molds, high labor consumption, increased slip moisture, substantial technological waste, etc. Articles produced by casting are more prone to deformation and crack formation. The quality of cast products to a large extent depends on compliance with special schedules of the complex process and on the rheological properties of the slip.

As is known, a slip is a steady suspension consisting of a finely dispersed, a dispersed, and a gaseous phase, where the finely dispersed phase liquefies upon introducing electrolytes into the clay – water system. Traditional electrolytes in producing ceramic slips are soluble glass (sodium silicate) and soda.

As clay disperses in a sodium silicate solution, a reaction takes place, as a consequence of which adsorbed Ca^{2+} ions precipitate in the form of insoluble calcium silicate and their positions are taken by Na^+ ions:

$$\text{Clay} - Ca^{2+} + Na_2SO_3 = \text{Clay}\begin{matrix} \diagup Na \\ \diagdown Na \end{matrix} + CaSiO_3.$$

The practice of using traditional electrolytes (soluble sodium silicate and soda) in slip preparation indicates that they have a narrow liquefying interval and delayed filtration. At the same time, separation of cast articles from gypsum molds is hampered, and the mold turnover decreases. All this inevitably leads to substantial waste at each process stage.

Along with traditional electrolytes, there currently exist thinners based on synthetic polymers, natural polyelectrolytes, etc. intended to control flow properties of disperse systems containing clay and kaolin, such as ceramic casting slips, including majolica slip.

Majolica slips based on polymineral clays, in contrast to porcelain slips, have increased moisture. The Gzhel' JSC uses slips of moisture over 50% when casting majolica products (the moisture of a porcelain slip is 31 – 33%). An increased water content in a majolica slip can be attributed to the mineral composition of low-melting clays, in which monmorillonites predominate, since their dilution require more water than known kaolinite clays.

In this context, decreasing moisture of majolica slips is a topical problem. During experiments, a nontraditional thinning agent was introduced into majolica slips, namely, 40% sodium polyacrylate (SPA), which is a synthesized organic compound categorized as an anion polymer for its capacity to dissociate in aqueous solutions.

SPA is a clear viscous liquid, ranging from green to dark green or, occasionally, yellow green; mass content of the main compound at least 36%, hydrogen ion activity of 1% solution ranging from 6.8 to 8.8 pH, is not explosive or fire-hazardous, is of low toxicity, has a sharp smell and a weakly irritant effect when applied to skin, does not age, and freezes in the cold.

The initial material for the production of acrylic polymers (polyacrylates) is acrylic acid. Depending its on polymerization conditions, this acid may form chain models of polyacrylic acid with different numbers of monomer segments:

$$-CH_2 - \underset{\displaystyle COOH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle COOH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle COOH}{\underset{|}{CH}} - \ .$$

The deflocculating effect of polyacrylates depends on their capacity for adsorption on the surface of mineral parti-

[1] Gzhel' State Art-and-Industrial Institute, Gus-Khrustalny, Vladimir Region, Russia.

0361-7610/04/0102-0021

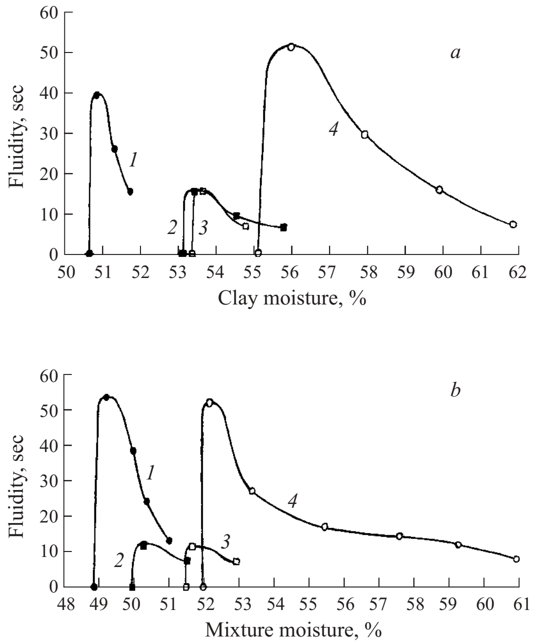

Fig. 1. Thinning variegated clay (*a*) and majolica mixture (*b*) with water of hardness 0 (*1*), 6.5 (*2*), 7.5 (*3*), and 12.0 mg · equ/liter (*4*).

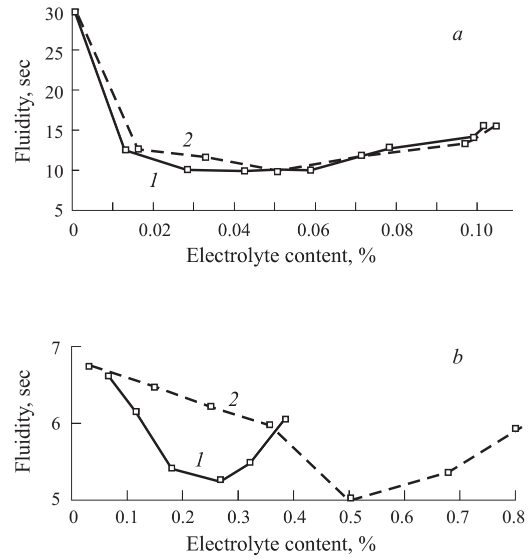

Fig. 2. The effect of 40% SPA (*1*) and sodium silicate solution (*2*) on fluidity of majolica (*a*) and clay (*b*) slips.

cles. An ionized polymer in an aqueous solution easily gets adsorbed on the surface of clay particles, imparting a negative charge to them. A positive charge zone surrounds the negatively charged particle. Such a double electron layer makes particles repel each other, which keeps the whole system in a dispersed state. The deflocculating properties of polyacrylates to a large extent depend on the polymer chain length.

Sodium polyacrylate has the following structure:

$$\mathrm{R-[-CH_2-\underset{\substack{|\\ COONa}}{CH}-]_n[-CH_2-\underset{\substack{|\\ COOH}}{CH}-]_mH}\ .$$

It can be seen that one hydrogen ion in the chain is replaced by a Na ion: $n + m = 80 - 140$, which corresponds to a molecular weight from 8000 to 15,000.

The capacity of SPA for dispersing argillaceous materials was analyzed by the known method [1] using clay from the Gzhel'skoe deposit and a majolica mixture of the following composition (wt.%): 60 variegated clay from the Gzhel'skoe deposit, 10 quartz sand, 20 nepheline-sienite, 10 clay from the Chasov'yarskoe deposit. The granulometric compositions of the clay and the mixture are listed in Table 1 [1].

TABLE 1

Material	Particle content, %, of size, μm*				Maximum particle size, μm
	< 1	1 – 5	5 – 10	10 – 20	
Variegated clay from Gzhel'skoe deposit	52.0	31.0	11.0	6.0	19.0
Majolica mixture produced by Gzhel' JSC	49.0	29.0	13.0	10.0	11.0

* There were no particles of sizes 20 – 40 and over 40 μm.

The necessity of studying the effect of water in the clay – water system is related to a modification of the properties of this system depending on the hardness of the water.

To perform experiments in thinning Gzhel'skoe clay and majolica mixture, water samples of different degrees of hardness (0, 6.5, 7.5, and 12.0 mg · equ/liter) were taken from different sites in the Gzhel' district.

Thinning variegated clay using water of different degrees of hardness demonstrated that as the hardness grows, the amount of water needed to impart mobility to the clay mixture increases (Fig. 1*a*). The first drop in the clay mixture mixed with distilled water emerges on reaching a moisture level of 50%. If the hardness of the water grows from 0 to 7.5 mg · equ/liter, the first drop is registered when the moisture is 53.2% and for a suspension mixed with water of hardness 12 mg · equ/liter the required moisture level is 55%.

Furthermore, based on the results of thinning Gzhel'skoe clay, the dependence of flow properties of slip on hardness of water is identified: the higher the hardness, the longer its flow time.

Experiments in dispersing a multicomponent majolica mixture produced by Gzhel' JSC were conducted according to the same schedule (Fig. 1*b*). The first drop in the majolica mixture suspension mixed with distilled water emerges on reaching a moisture level of 48.8%, i.e., 1.2% lower than in the clay suspension. An increase in hardness of water from 6.5 to 7.5 mg · equ/liter increases moisture from 51.3 to 51.8%.

Comparing the experimental results obtained, the following conclusions can be made: Gzhel'skoe clay and majolica

mixture can be thinned using water of different degrees of hardness. Variation in water hardness leads to variations in moisture and casting properties. A dependence of increasing moisture of suspensions on increasing hardness of water was established. A smaller amount of water required to dilute the majolica mixture compared with clay can be attributed to a lower content of argillaceous materials in the majolica mixture.

Thus, it is significantly more difficult to dilute pure clays than mixtures containing the same clays in smaller quantities besides other materials. Furthermore, ceramic production requires strict monitoring of hardness of water in slip preparation, since with increasing hardness the moisture may increase and the flow properties of the slip may change.

Preliminary results on liquefying mixtures using water of different degrees of hardness were taken into account in studying the effect of a new thinning agent, i.e., 40% SPA on the flow properties of majolica slip mixed with water of hardness 7.5 mg · equ/liter.

The optimum thinning of the multicomponent majolica mixture was achieved using 40% SPA in an amount of 0.043%, with slip moisture 50.2% (Fig. 2*a*). A further introduction of this diluent leads to thixotropic phenomena. The traditional electrolyte, i.e., sodium silicate solution, causes thixotropic phenomena in slip when contained in an amount of 0.05% with moisture 51.1% and has a narrower thinning interval than the slip containing 40% SPA.

Experiments in thinning polymineral clays from the Gzhel'skoe deposit using a traditional electrolyte (sodium silicate solution) and 40% SPA revealed a change in the thinning process. It can be observed in Fig. 2*b* that thinning variegated Gzhel'skoe clay mixed with water of hardness 7.5 mg · equ/liter depends on the type of the thinner. Thus, using 40% SPA allows for dispersing the clay mixture when its content is 0.10 – 0.26%, whereas sodium silicate solution does that when its content in the clay mixture is 0.50%.

The results obtained in thinning majolica mixture and Gzhel'skoe clay show that the effect of 40% SPA on the clay from the Gzhel'skoe deposit is more perceptible than on the majolica mixture. The quantity of 40% SPA required for thinning Gzhel'skoe clay is nearly half as much as the quantity of sodium silicate solution.

Thinning majolica mixtures using 40% SPA insignificantly decreases the moisture of the slip, i.e., by about 1% and reduces the content of electrolyte by 0.01% compared with sodium silicate solution.

TABLE 2

Slip	Duration of staying in mold, min	Rate of casting, g/(cm^2 · min)	Dry sample thickness, mm	Existence of defects
Based on multicomponent majolica mixture with:				
40% SPA (0.043%)	3	0.14	4.5	–
	1	0.32	2.0	–
sodium silicate solution (0.051%)	3	0.18	5.5	Crack formation
	1	0.39	2.3	–
Based on polymineral clay from Gzhel'skoe deposit with:				
40% SPA (0.267%)	3	0.14	3.8	–
	5	0.09	5.0	–
sodium silicate solution (0.051%)	3	0.17	5.1	Crack formation

The casting rate of slips containing 40% SPA and sodium silicate solution was determined by the crucible method. The thickness of cast samples was 2 – 6 mm. It was found that samples of thickness 4.5 – 5.5 mm can be produced from a majolica slip with sodium silicate solution or 40% SPA at a casting increment rate of 0.14 or 0.180 g/(cm^2 · min) and samples of thickness 2.0 – 2.3 mm made from slip with a casting rate of 0.32 or 0.39 g/(cm^2 · min). The quality of cast sample satisfied technical requirements imposed on majolica products, except for some articles produced from majolica slip with sodium silicate solution, which had cracks.

We were not able to produce high-quality articles from a clay slip with sodium silicate solution (Table 2). However, articles made from the clay slip with 40% SPA of thickness 4 mm exhibited a uniform thickness and low deformation in casting and drying, and the casting increment rate was 0.14 g/(cm^2 · min).

Thus, the use of 40% SPA as a thinner for majolica slip replacing the traditional electrolyte will make it possible to improve the flow properties of the slip, expand the liquefying interval, and insignificantly decrease the slip moisture, which will contribute to improving the quality of articles produced by casting.

The optimum content of 40% SPA recommend for thinning polymineral clay from the Gzhel'skoe deposit is 0.267% (slip moisture 54.2%) and for majolica mixture 0.043% (slip moisture 50.2%) for water hardness 7.5 mg · equ/liter.

REFERENCES

1. E. S. Lukin and N. T. Andrianov, *Technical Analysis and Control of Ceramic Production* [in Russian], Moscow (1980).